NASA Technical Memorandum 83779

# The Friction Behavior of Semiconductors Si and GaAs in Contact With Pure Metals

Hiroshi Mishina Lewis Research Center Cleveland, Ohio

Prepared for the International Tribology Conference sponsored by the Japan Society of Lubrication Engineers Tokyo, Japan, July 8-10, 1985



# THE FRICTION BEHAVIOR OF SEMICONDUCTORS ST AND GAAS

## IN CONTACT WITH PURE METALS

#### Hiroshi Mishina\*

National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135

#### SUMMARY

The friction behavior of the semiconductors silicon and gallium arsenide in contact with pure metals was studied. Five transition and two nontransition metals, titanium, tantalum, nickel, palladium, platinum, copper, and silver, slid on a single crystal silicon (111) surface. Four metals, indium, nickel, copper and silver, slid on a single crystal gallium arsenide (100) surface. Experiments were conducted in room air and in a vacuum of  $10^{-7}$  N/m<sup>2</sup> ( $10^{-9}$  torr).

The results indicated that the sliding of silicon on the transition metals exhibited relatively higher friction than for the nontransition metals in contact with silicon. There was a clear correlation between friction and Schottky barrier height formed at the metal-silicon interface for the transition metals. Transition metals with a higher barrier height on silicon had a lower friction. The same effect of barrier height was found for the friction of gallium arsenide in contact with metals.

#### INTRODUCTION

The physical and chemical properties of contacting materials play a dominant role in the tribological phenomena of solids. Considerable studies have been conducted for metal-metal contacts. Melting point and crystal structure of metals affect the adhesive behavior (ref. 1). Friction and wear of metals are closely related to mutual solubility of two mating metals (refs. 2 to 4). Only a few tribological experiments for metal-semiconductor contacts, however, have been conducted. Although the nature of surface fracture, friction and wear were studied for silicon and germanium in contact with metals (refs. 5 to 7), the effects of the physical properties of the metal-semiconductor interface on tribological behavior have not been examined in detail.

When a semiconductor comes into contact with a metal the surface state is remarkably different from the metal-metal interface. A barrier is formed by a bending of electron band near the semiconductor surface and the nature of the barrier height is one of the most important factors in the characterization of the metal-semiconductor interface. Although in the first model proposed by Schottky (ref. 8) and Mott (ref. 8) the barrier height depended on the metal work function and the electron affinity of semiconductors, experimental

<sup>\*</sup>The Institute of Physical and Chemical Research, Wako-shi Saitama, Japan and NRC-NASA Research Associate.

results did not coincide with this model. For this discrepancy Bardeen (ref. 10) put forward another explanation for semiconductor surface-state. According to his concept, the barrier height was restricted by the presence of a insulating surface film and it was almost independent of the contacting metal. Subsequent experiments, however, measuring the precise barrier height at the metal-semiconductor interface revealed that the barrier height was dependent upon the metal although it had weaker correlation than predicted in the Schottky-Mott model (refs. 11 to 19). These results indicated that the barrier height was complicatedly related to chemical and physical properties of both metal and semiconductor. The relation of the barrier height to many factors, such as the heat of formation of metal silicides (ref. 20), the eutectic temperature of transition metal silicides (ref. 21), and the chemical bonding of metal-silicon interface (ref. 22), have been recently discussed for silicon in contact with the transition metals.

The objective of this investigation was to determine the effect of barrier height at the metal-semiconductor interface on the tribological behavior of the semiconductor. In a recent experiment examining the doping effect for silicon, friction behavior was sensitively affected by the P- or N-type electron state of silicon in contact with gold metal (ref. 6). In this paper the friction behaviors of silicon and gallium arsenide in sliding contact with pure metals in high vacuum and in room air were studied. The friction behavior for each semiconductor is discussed with reference to the properties of metal-semiconductor interface.

## MATERIALS

The semiconductors used in this experiment were silicon and gallium arsenide. Silicon was a single crystal plate of the (111) orientation. Gallium arsenide was an undoped single crystal plate of the (100) orientation. Both of the specimens were polished and the surface roughnesses were  $R_{\mbox{\scriptsize max}}$  less than 0.01  $\mu\mbox{\scriptsize m}$ .

Metals used as pin specimens were pure polycrystalline titanium, tantalum, nickel, palladium, platinum, indium, copper and silver. Five transition metals Ii, Ta, Ni, Pd and Pt, and two nontransition metals, Cu and Ag, slid on the Si (III) surface parallel to the [II2] crystallographic direction. Four metals, In, Ni, Cu and Ag slid on the GaAs (100) surface parallel to the [OII] direction. The diameter of each pin specimen was 3.18 mm and the sliding surface was hemispherical in shape. The sliding surface was polished with 0.3  $\mu m$  aluminum powder. Both pin and plate specimens were cleaned with ethyl alcohol in an ultrasonic cleaner before each experiment.

## EXPERIMENTAL METHOD

Two different apparatuses were used for the experiments. Both apparatuses were pin and plate type devices. In the experiment in room air, load with weights of 0.1 to 1.0 N was applied to the pin specimen. A semiconductor specimen was mounted to a stage which moved in reciprocating motion with a 10 mm stroke. The moving speed was 1.4 mm/s in both directions. In each experiment the pin specimen slid on the same 10 mm path of the semiconductor surface 30

times in each direction. The experiments were conducted in room air and room temperature (21°  $\sim$  23° C, 30  $\sim$  35 percent relative humidity).

The apparatus used for the experiments in vacuum was contained in a vacuum system. A pin specimen was contained on a beam projected into the vacuum system. The beam had two flats mounting strain gages in order to measure the load and the friction force. The semiconductor specimen was mounted on a ceramic block (thermal and electrical insulator) contained at the end of a manipulator beam. One surface of the block was coated with a hafnium sputtered film in order to achieve sputtering and heating of the semiconductors. A chromel-alumel thermocouple buried just under the semiconductor specimen was used for measuring the temperature when the specimen was heated. Load applied by manipulating the block towards the pin was measured by a strain gage. The load applied was 0.1 N. The pin specimen slid a single path of 12 mm stroke on the semiconductor surface. Sliding velocity was 0.2 mm/s. The vacuum system was a conventional vacsorb and ion pumped system achieving a pressure of  $10^{-7}$  N/m² as measured by a nude ionization gage.

#### EXPERIMENTAL PROCEDURE IN THE VACUUM SYSTEM

After the specimens were placed in the vacuum chamber, the system was evacuated. The system was baked out overnight at 260° C (150° C in the case of indium pin), after which the pressure was in the  $10^{-7}$  N/m² range. Argon gas was bled into the vacuum system to a pressure of  $10^{-1}$  N/m². A 1000 V direct current potential was applied to the specimen and it was sputter bombarded for a period of 30 min. Since Si and GaAs are semiconductors, when they were sputtered a direct current potential was applied to a hafnium sputtered film on the ceramic block to achieve sputtering of the specimens.

Since the argon sputter bombardment of the GaAs produces changes in the initial surface composition (refs. 23 to 25), the cleaning method of GaAs was different from that of Si and metals. A sputtering and annealing method was used in the experiment with GaAs (refs. 24 and 25).

After argon gas was bled into the system to a pressure of  $10^{-1}$  N/m², a 300 V direct current potential was applied for a period of 30 min. The system was evacuated again to a pressure of  $10^{-6} \sim 10^{-7}$  N/m². The GaAs was annealed at 520°  $\sim 550^{\circ}$  C for a period of 60 min. The GaAs specimen was heated indirectly by a resistance heating of the hafnium film coated on the ceramic block. All friction experiments were conducted with the system reevacuated to a pressure of  $10^{-7}$  N/m² ( $10^{-9}$  torr).

#### RESULTS AND DISCUSSION

## Friction With Silicon

The correlation of coefficient of friction with load for five transition and two nontransition metals slid on the Si (111) surface in room air are presented in figure 1. In table I coefficients of friction in vacuum and in room air at a load of 0.1 N are summarized. A stick-slip motion was found for all metals slid on silicon except for the two nontransition metals in room air. Coefficients of friction presented in the figure and the table are the

maximum values measured in each experiment. As exhibited in figure 1 and table I the friction of silicon was sensitive to the contacting metals. Ti exhibited the highest friction among the seven metals. With the other four transition metals, friction was lower. The two nontransition metals, Cu and Ag, exhibited very low friction. The influence the metal exerted on the friction behavior did not change when the load varied from 0.1 to 1.0 N. The effect of load on the coefficient of friction was similar for all metals except Ag. The friction was higher when a smaller load was applied. In vacuum the correlation between coefficient of friction and metal was similar to that in room air.

Silicon is well known to be a highly polarizable semiconductor and it has a strong chemical activity with the transition metals and forms one or more compounds with these metals (refs. 20 and 22). These characteristics closely relate to the formation of an intimate contact at the interface. Hence, the transition metal with a high chemical affinity for silicon tends to give a relatively high friction. Since the nontransition metals, on the other hand, have low chemical activity for silicon, they do not form strong bonding at the interface. This characteristic resulted in a low friction for nontransition metals in contact with silicon. The transition metals exhibiting a similar chemical character toward silicon, were examined more precisely to clarify a possible correlation of friction with barrier height.

Figure 2 indicates the coefficient of friction in room air as a function of barrier height for the transition metals on a chemically etched silicon surface. From Ti (barrier height  $\varphi_b=0.50$  eV) to Pt ( $\varphi_b=0.81$  eV), the coefficient of friction gradually decreased with increasing barrier height. The same relation between barrier height and coefficient of friction in vacuum is presented in figure 3 for both chemically etched and cleaved surfaces. A sputter cleaned surface will be considered the same as a cleaved surface as for the barrier height. However, since the measurements of barrier height on cleaved surfaces were not completed for Ti and Ta, the results for these two metals are not shown in figure 3. For three metals, Ni, Pd and Pt, there was a similar effect of barrier height with both surface preparations.

As indicted in figures 2 and 3, the coefficient of friction was strongly dependent upon the barrier height formed at the interface. Metals with a higher barrier height on silicon had a lower friction. There was a linear correlation between coefficient of friction and barrier height. Since the presence of surface films masked the genuine character of the metal-silicon interface, the effect of barrier height was weaker in room air.

Figure 4 is a wear track on the silicon surface in sliding contact with Ti in vacuum. The resulting strong bonding at the interface produced many particles adhering on the wear track (fig. 4(a)). Figures 4(b) and (c) present enlarged micrographs of particles and Ti-K $_{\alpha}$  X-ray map. The debris was not metallic titanium but silicon particles, which had been torn off from the original silicon surface in the first stage and then subsequently back-transferred to the silicon surface. Similar silicon particles were observed on other wear tracks on silicon in sliding contact with metals.

## Friction With Gallium Arsenide

Figure 5 indicates the coefficient of friction for In, Ni, Cu and Ag slid on a GaAs (100) surface in room air. The results of friction experiments at a load of 0.1 N in room air and in vacuum are summarized in table III. Since a stick-slip motion was found in the friction for all metals in vacuum and for indium in room air, maximum values are presented in the figure and the table. The coefficient of friction for In was the highest among four metals. With Cu and Ag, the frictions were lowest and there was little difference between them. The friction was even less for all metals when the smaller load was applied in room air. The influence of contacting metal on the friction behavior of gallium arsenide in vacuum was similar to that observed in room air.

Figure 6 indicates the coefficient of friction in room air as a function of barrier height on chemically etched gallium arsenide at loads of 0.1 and 1.0 N. The same correlation between the barrier height and the coefficient of friction in vacuum is presented in figure 7. In figure 7 coefficients of friction are plotted against both chemically etched and cleaved surfaces except for nickel. The influence of surface preparation on the correlation were not different from each other. As exhibited in these figures the coefficient of friction for gallium arsenide was dependent upon the barrier height. Indium with the lowest barrier height had the highest coefficient of friction. Silver exhibited the lowest friction as a result of the very high barrier height. These effects of barrier height on friction appeared more clearly when the surface films were absent from the sputtered surfaces in vacuum. Although the effect of barrier height of gallium arsenide was found to be similar to that of silicon in figure 3, the relation was not linear as with silicon in contact with the transition metals.

Figure 8 is a wear track on GaAs in sliding contact with indium in vacuum. The wear track surface of gallium arsenide was quite different from that of silicon. The sliding surface was rough and a large quantity of particle transfer was observed on the wear track (fig. 8(a)). The result of X-ray analysis indicated that the debris on the wear track were transferred particles of indium (figs. 8(b) and (c)). Since weak bonding occurred at the interface, very little surface fracture of gallium arsenide was observed with the other metals sliding on gallium arsenide.

## CONCLUSIONS

The sliding friction behavior of the semiconductors Si and GaAs in contact with pure metals was studied. From experiments in room air and in vacuum, the following points are made:

- (1) The coefficient of friction for the semiconductors were sensitive to the contacting metal. In the friction of silicon, the transition metals exhibited higher friction than the nontransition metals, which was directly related to the strong chemical affinity of transition metals for silicon.
- (2) With silicon in contact with transition metals, the friction behavior was strongly dependent upon the barrier height formed at the interface. A similar effect of barrier height was found for friction of gallium arsenide in contact with metals.

- (3) In room air the effect of barrier height was weaker for both silicon and gallium arsenide. The presence of surface films masked the real character of the metal-semiconductor interface.
- \(4\) In contrast to a silicon surface in contact with titanium, where many silicon particles were observed on the wear track, a transfer of large quantity of indium was found on the gallium arsenide surface when indium slid on gallium arsenide in vacuum.

#### REFERENCES

- 1. Sikorski, M. E.: Wear, 7, 144 (1964).
- Rabinowicz, E.: ASLE Trans., 14, 198 (1971).
- 3. DeGee, A. W. J.: The Friction of Gold-Silver Alloys Against Steel. Wear, vol. 8, no. 2, 1965, p. 121.
- 4. Sasada, T.; Norose, S.; and Mishina, H.: The Behavior of Adhered Fragments Interposed Between Sliding Surfaces and the Formation Process of Wear Particles. Trans. ASME, J. of Lubrication Technology, vol. 103, April 1981, p. 195.
- 5. Stickler, R.; and Booker, G. R.: Surface Damage on Abraded Silicon Specimens. Phil. Mag., vol. 8, 1963, p. 859.
- 6. Buckley, D. H.; and Brainard, W. A.: Adhesion and Friction of Iron and Gold in Contact with Elemental Semiconductors. NASA TN D-8394, Jan. 1977.
- 7. Mishina, H.; and Sasada, T.: Mild Wear Occurring in Pure Metal/Semiconductor Rubbings. Proc. 25th Japan Congress on Materials Research, The Society of Materials Science, Japan, 1982, p. 139.
- 8. Schottky, W.: Zur Halbleitertheorie der Sperrschicht-und Spitzengleichrichter. Zeits. Physik, vol. 113, 1939, p. 367.
- 9. Mott, N. F.: The Theory of Crystal Rectifiers. Proc. Roy. Soc. (London), vol. Al71, 1939, p. 27.
- 10. Bardeen, J.: Surface State and Rectification at a Metal Semi-Conductor Contact. Phys. Rev., vol. 71, no. 10, 1947, p. 717.
- 11. Cowley, A. M.: Titanium-Silicon Schottky Barrier Diodes. Solid State Electronics, vol. 13, 1970, p. 403.
- 12. Landkammer, F. J.: Barrierenhohen von Metall-Halbleiterkontakten. Solid State Commun., vol. 5, 1967, p. 247.
- 13. Jäger, H.: and Kosak, W.: Die Metall-halbleiten-kontaktbarrieren der Metalle aus des Neberngruppe I und VIII auf Silizium und Germanium. Solid State Electronics, vol. 12, 1969, p. 511.
- 14. Turner, M. J., and Rhoderick, E. H., Solid State Electron., 11, 291 (1968).
- 15. Hirose, M., Altaf, N. and Arizumi, T., Jap. J. Appl. Phys. 9, 260 (1970).
- 16. Archer, R. J.; and Atalla, M. M.: Metal Contacts on Cleaved Silicon Surfaces. Ann. N. Y. Acad. Sci., vol. 101, 1963, p. 697.
- 17. Seirangan, G. B.; and Tkhorik, Y. A.: On the Schottky Barrier Height of Metal-GaAs System. Phys. Status Solidi. Vol. Al3, 1972, p. Kll5.
- Smith, B. L.: The Effect of Surface Treatment on Gallium Arsenide Schottky Barrier Diodes. Ph.D. Thesis, Manchester University, 1969.
- 19. Spitze, W. G.; and Mead, C. A.: Barrier Height Studies on Metal Semiconductor Systems. J. Appl. Phys., vol. 36, 1963, p. 3061.

- Andrews, J. M.; and Phillips, J. C.: Chemical Bonding and Structure of Metal-Semiconductor Interfaces. Phys. Rev. Lett., vol. 35, no. 1, 1975, p. 56.
- 21. Ottaviani, G.; and Tu, K. N.: Interfacial Reaction and Schottky Barrier in Metal-Silicon Systems. Phy. Rv. Lett., vol. 44, no. 4, 1980, p. 284.
- 22. Ho, P. S. Chemical Bonding and Schottky Barrier Formation at Transition Metal-Silicon Surfaces. J. Vac. Sci. Technol., vol. A1, no. 2, 1983, p. 745.
- 23. McGuire, G. E.: Effects of Ion Sputtering on Semiconductor Surfaces. Surface Science, vol. 76, 1978, p. 130.
- 24. Mark, P.; Pianetta, P.; Lindau, I.; and Spicer, W. E.: A Comparison of LEED Intensity and Data from Chemical Polished and Cleaved GaAs (110) Surfaces. Surface Science, vol. 69, 1977, p. 735.
- 25. Kübler, B.; Ranke, W.; and Jacobi, K.: LEED and AES of Stoichiometric and Arsenic-Rich GaAs (110) Surfaces Prepared by Molecular Beam Epitaxy. Surface Science, vol. 92, 1980, p. 519.

TABLE I. - COEFFICIENT OF FRICTION FOR METALS SLID ON SILICON IN VACUUM AND ROOM AIR, LOAD 0.1 N

Metal	In vacuum, 10 <sup>-7</sup> N/m <sup>2</sup>	In room air
Titanium Tantalum Nickel Palladium Platinum Copper Silver	7.3 6.7 5.2 4.0 3.2 3.0 3.1	0.73 .68 .60 .41 .30 .25

TABLE II. - COEFFICIENT OF FRICTION FOR METALS SLID ON GaAS IN VACUUM AND ROOM AIR, LOAD 0.1 N

Metal	In vacuum, 10 <sup>-7</sup> N/m <sup>2</sup>	In room air
Indium	3.2	0.38
Nickel	1.3	.23
Copper	1.0	.18
Silver	0.91	.17

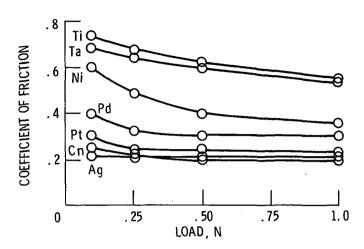


Figure 1. - Coefficient of friction versus load for metals slid on Si (111) surface in room air, v = 1.4 mm/s.

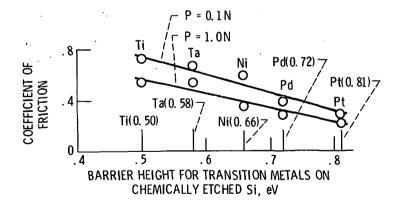


Figure 2. - Relationship between coefficient of friction and barrier height for transition metals on chemically etched Si surface [11-15] in room air, P = 0.1 and 1.0 N, v = 1.4 mm/s.

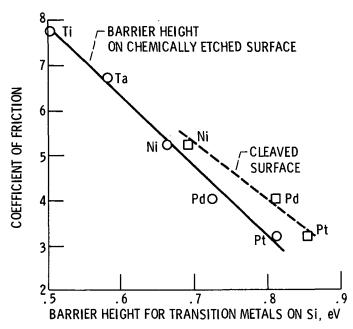


Figure 3. - Relationship between coefficient of friction and barrier height for transition metals on etched (0) [11-15] and cleaved (X) [16] Si surface in  $10^{-7}$  N/m<sup>2</sup>, P = 0.1 N, v = 0.2 mm/s.



Figure 4. - Wear track of Si (111) surface in sliding contact with titanium in  $10^{-7}$  N/m<sup>2</sup>, P = 0.1 N, v = 0.2 mm/s.

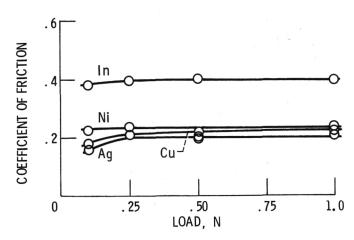


Figure 5. - Coefficient of friction versus load for metals slid on GaAs (100) surface in room air, v = 1.4 mm/s.

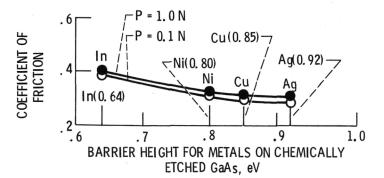


Figure 6. - Relationship between coefficient of friction and barrier height for metals on chemically etched GaAs surface[17-18]in room air, P = 0.1 and 1.0 N, v = 1.4 mm/s.

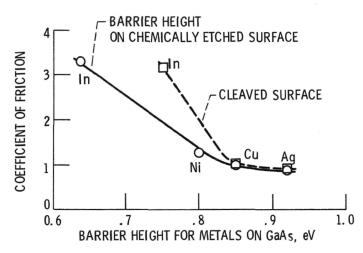


Figure 7. - Relationship between coefficient of friction and barrier height for metals on etched (0)[17-18] and cleaved (X)[18-19] GaAs surface in  $10^{-7}$  N/m<sup>2</sup>, P = 0.1 N, v = 0. 2 mm/s.

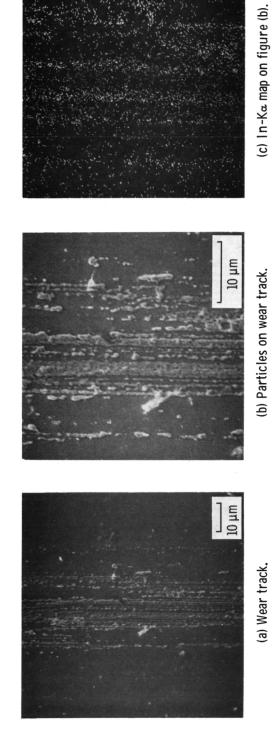


Figure 8. - Wear track of GaAs (100) surface in sliding contact with indium in  $10^{-7}$  N/m<sup>2</sup>, P = 0.1 N, v = 0.2 mm/s.

1. Report No.	2. Government Accession	No. 3.	Recipient's Catalog No.		
NASA TM-83779					
4. Title and Subtitle		5.	Report Date		
The Friction Behavior of Semiconductors Si and GaAs in Contact With Pure Metals			6. Performing Organization Code		
			506-53-1B		
7. Author(s)			8. Performing Organization Report No.		
Hiroshi Mishina			E-2228		
			10. Work Unit No.		
9. Performing Organization Name and Address		11.	11. Contract or Grant No.		
National Aeronautics and S	pace Administrati				
Lewis Research Center Cleveland, Ohio 44135			12 Type of Beautierd Build Const		
			13. Type of Report and Period Covered		
12. Sponsoring Agency Name and Address			Technical Memorandum		
National Aeronautics and S Washington, D.C. 20546	pace Administrati	on 14.	Sponsoring Agency Coo	ie e	
washington, D.C. 20340					
15. Supplementary Notes					
Hiroshi Mishina, The Insti	tute of Physical	and Chemical Res	search, Wako-sl	hi Saitama,	
Japan and NRC-NASA Researc Conference sponsored by th	h Associate. Pre	epared for the li	nternational Ti	ribology	
July 8-10, 1985.	e Japan Sucrety (	or Lubrication E	ngineers, loky	o, Japan,	
16. Abstract					
			11:	·	
The friction behavior of t tact with pure metals was	ne semiconductors	s Sillicon and ga cansition and two	o nontransitio	n metals.	
titanium, tantalum, nickel	. palladium. pla	tinum, copper, a	nd silver, sli	d on a	
single crystal silicon (11	1) surface. Four	r metals, indium	, nickel, copp	er and	
silver, slid on a single c	rystal gallium a	rsenide $(100)$ su	rface. Experi	ments	
were conducted in room air indicated that the sliding	and in a vacuum	of $10^{-7}$ N/m <sup>2</sup> (1	U <sup>-3</sup> torr). In	e results rela-	
tively higher friction tha	n for the nontra	nsition metals i	n contact with	silicon.	
There was a clear correlat	ion between fric	tion and Schottk	y barrier heig	ht formed	
at the metal-silicon inter	face for the tra	nsition metals.	Transition me	tals with	
a higher barrier height on rier height was found for	silicon had a l	ower friction.	in contact wi	t of Dar- th	
metals.	the friction of	garrium arseniue	III COIICACE WI		
17. Key Words (Suggested by Author(s))		18. Distribution Statement			
Friction	Unclassified - unlimited				
Silicon	STAR Category 27				
Gallium arsenide					
19. Security Classif. (of this report)	20. Security Classif. (of this	page)	21. No. of pages	22. Price*	
Unclassified	Unclassified				

National Aeronautics and Space Administration

Washington, D.C. 20546

Official Business
Penalty for Private Use, \$300

SPECIAL FOURTH CLASS MAIL BOOK





Postage and Fees Paid National Aeronautics and Space Administration NASA-451

NASA

POSTMASTER:

If Undeliverable (Section 158 Postal Manual) Do Not Return